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**MEASUREMENT OF CONDENSATE FILM CONTAMINATION  
ON CRITICAL SURFACES BY CHARGED PARTICLE  
EXCITED X-RAY FLUORESCENCE***W. P. Saylor, General Electric Company, Valley Forge, Pa.*

## ABSTRACT

A unique technique was developed by the General Electric Co. for the determination of trace quantities of a hydrocarbon film contaminant on critical surfaces by a charged particle excited x-ray fluorescence method. The method was successfully employed for constructing an instrument to be used to measure condensate contaminants deposited on optical and thermal control surfaces of the Nimbus 5 spacecraft after environmental testing. Data is presented showing the measured thicknesses of hydrocarbon film condensed during the environmental testing period. Measurements were also used to establish the effective removal of these contaminant films. As an extension of this technology, modifications of the device are presently being made for application of in-situ contamination monitoring during thermal-vacuum environmental testing of a spacecraft.

INTRODUCTION

Contamination of critical spacecraft surfaces and its corresponding effect upon spacecraft performance has long been of mutual concern to both NASA and the General Electric Co. Spacecraft subsystems and experiment malfunctions and failures experienced during both environmental system test activity and actual flight performance, which have been determined to be directly attributable to contamination, have emphasized the need to determine, control, and maintain the cleanliness of critical surfaces.

Hydrocarbon film contamination of less than 1000A° in thickness on critical optical and/or thermal control surfaces can be produced as a result of outgassing by-products. These thin films are frequently not visible to the eye and cause no reasonable changes to the original sensor optical characteristics. In space, however, exposure of these surfaces to short wavelength UV or low energy ionizing radiation can cause coloration of these thin films resulting in deleterious changes to original sensors performance. A large part of this hydrocarbon contamination may well be deposited during ground handling operations. In order to minimize or eliminate these contamination problems it became necessary to institute a system to detect thin organic film contaminants to insure operational integrity of the critical component prior to launch. In addition, the detection system will also be used to establish contaminant origin, if possible, as well as to insure effective removal of the contaminant by an established cleaning procedure.

## Measurement Technique

The method by which condensate film thicknesses are to be measured is by a unique X-ray fluorescence technique. X-ray fluorescence is used quite extensively in industry for trace elemental analysis. The sensitivity of the method is such that elemental concentration of less than 10 nanograms can easily be detected. The method is nondestructive, insensitive to the geometry or stoichiometry of the polymer films and is not susceptible to environmental effects. In addition, instrumentation for the method is relatively simple and can be made small in size and easily portable.

The principle by which the measurement technique operates is based on detecting the carbon characteristic x-rays (280 ev) generated by alpha-particle induced fluorescence of the hydrocarbon contaminant film on a given substrate. Alpha-particles are well suited for exciting the thin hydrocarbon film in that they have low penetrating powers, yet produce high fluorescent X-ray yields for low atomic number target elements.<sup>(1,2)</sup> Perhaps, the most important feature is the fact that little or no bremsstrahlung continuum x-radiation is generated in the slowing processes of the alpha-particles resulting in low background counting rates which aids in the systems overall sensitivity. Figure 1 shows the basic layout. A low level radioisotopic source of polonium emits alpha particles. These particles bombard the inorganic substrate. If there is a thin layer of carbon bearing contaminate deposited on the substrate, characteristic x-rays due to carbon (44 Å) are generated. These x-rays are sensed in a x-ray sensor which converts them into electronic pulses. The electronic pulses are amplified and counted for a fixed time interval, typically 10 - 100 seconds. The number of counts is then directly proportional to the number of carbon atoms deposited and hence directly proportional to the thickness of the contaminated layer. The sensitivity of the method is derived as follows: The total number of output counts detected in a channel corresponding to A atoms of an element in a thin sample is given by,

$$N = A n \sigma \omega K (\Omega/4\pi) \epsilon$$

where n is the total number of alpha particles per cm<sup>2</sup>,  $\sigma$  the cross section for ionization for the shell in question,  $\omega$  the fluorescence field, K the relative transition probability for the particular x-ray peak, used in the measurement,  $\Omega$  the solid angle subtended by the detector and  $\epsilon$  the efficiency of the detector. One can now substitute numerical values for all these factors to compute an order-of-magnitude value of sensitivity for a given amount of condensate on a substrate surface.

### Sample Thickness Computation

For a 100-angstrom-thick layer of a typical hydrocarbon contaminate

such as dioctyl phthalate, the total number of carbon atoms  $A$  equals  $2.92 \times 10^{17}$ . The cross section  $\sigma = 2 \times 10^5$  (Reference 3) Barns,  $\omega = 1.2 \times 10^{-3}$  (Reference 4) and  $K = 1$ . The factor  $\Omega/4\pi$  is equal to  $2 \times 10^{-2}$  for good geometry. Detector efficiency is assumed at 20-percent. A 10 mC alpha source is used which results in a flux of  $1.45 \times 10^7$  alphas -  $\text{cm}^{-2} - \text{sec}^{-1}$ . For a measuring period of 100 seconds the total intensity  $N$  is then  $= (2.92 \times 10^{17})(2 \times 10^{-19})(1.2 \times 10^{-3})(1)(2 \times 10^{-2})(0.2)(1.45 \times 10^7)(10^2)$  or  $N = 406$  counts. The predicted accuracy, as limited by statistical variations ( $3\sigma$  limits), is then  $100 \pm 15$  angstroms. The minimum detectable thickness will be limited by instrumental background and counting rate statistics.

### Constructional Parameters of The Sensor

Figure 2 shows a schematic of the contamination sensor head construction. A standard 5 millicurie polonium - 210 alpha-particle source(5) is used to bombard the interested substrate. If a condensate film is present, the carbon-K X-rays generated by excitation with the alpha-particles are isolated and detected by a thin-window P-10 gas flow proportional counter. The proportional counter is of standard construction except for the entrance window. The entrance window was constructed of aluminized polypropylene stretched to a thickness of one micron. This yielded a detection efficiency for carbon-K X-rays of 50%. A 5 micron thick stretched polypropylene filter was used to help isolate the carbon-K X-rays in the presence of a oxygen and nitrogen generated x-ray background. The alpha-source is so shielded such that the proportional counter cannot see the source directly. The entire region surrounding the alpha source, proportional counter and surface being analyzed is bathed in a helium atmosphere. The helium atmosphere is required to overcome the extremely short mean free path of the carbon-K X-rays in air.

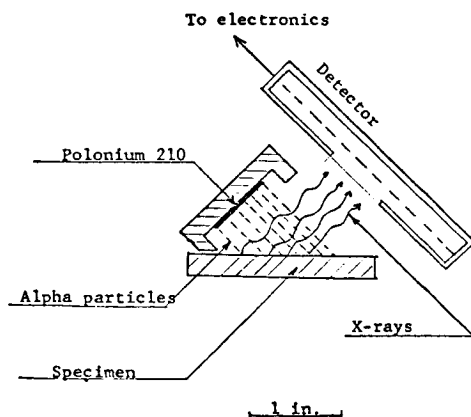


Figure 1, Basic Layout of Sensor System

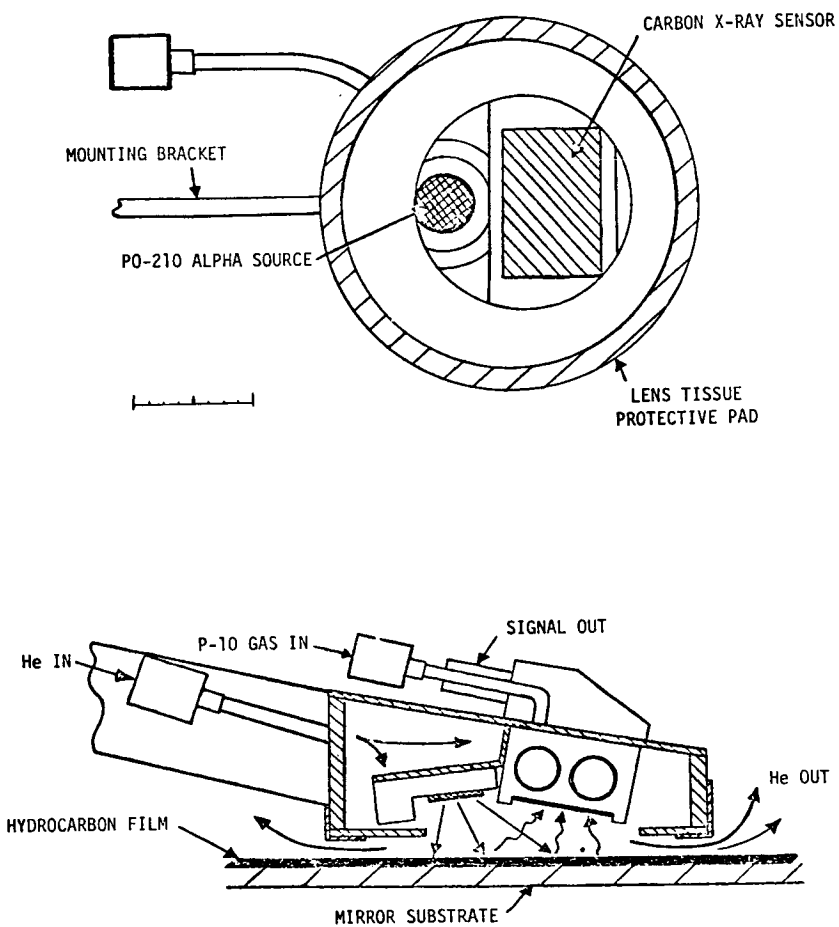


Figure 2, Schematic Diagram of the Contamination Sensor

The carbon-K x-rays detected by the sensor are isolated by a combination of the 5 micron polypropylene filter and energy discrimination in the proportional counter. A preamplifier is used to amplify the pulses from the proportional counter and drive the signal cable to the remainder of the processing electronics located remotely. The proportional counter is operated in the pulse counting mode, and coupled with the high gain of the unit makes the system insensitive to variations in electronic gain and power supply voltage drift. The constructed sensor has a sensitivity that lies in the hydrocarbon film thickness range of 50 to 10,000Å°, and the device can detect a hydrocarbon film of less than 100Å° in thickness in a response time of 100 seconds as established through calibration. Figure 3 shows a photograph of the constructed contamination monitor sensor head.

#### Calibration of sensor

Thin polymer films of "formvar" ranging in thickness from 200 to 2000Å° were created for use as hydrocarbon film thickness calibration of the contamination sensor. The formvar films were made by dissolving 2 grams of formvar powder in 100 ml of ethylene dichloride solvent. One or more drops of the solution, depending on the film thickness desired, were then spread on a large tray of water and allowed to dry. The resulting film was then picked off the water surface by an aluminum wire screen substrate. The thickness of each of the formvar films used for calibrating were measured by x-ray transmission techniques. The mesh supported thin polymer films were placed directly in front of an x-ray sensor. The monochromatic x-ray line used for the measurement was that of nitrogen-K $\alpha$  at 31.68Å°. The line was generated by alpha-particle x-ray fluorescence excitation of pure nitrogen gas at atmospheric pressure. The x-ray line intensity was measured with and without the thin formvar films present in front of the sensor. The intensity ratio then is proportional to the film thickness. Table I gives the measured results of the calibration films x-ray transmissions at 31.68Å°.

TABLE I  
Measured Film Transmissions

No. 1	Aluminum support mesh only	19540 C/100 sec.	
No. 2	Mesh plus thin formvar film 1	18550	95%
No. 3	Mesh plus thin formvar film 2	17020	87%
No. 4	Mesh plus thin formvar film 3	14462	74%
No. 5	Mesh plus polypropylene film 4	1804	8.6%
No. 6	Mesh plus 1 mil thick polypropylene 5	140	Background

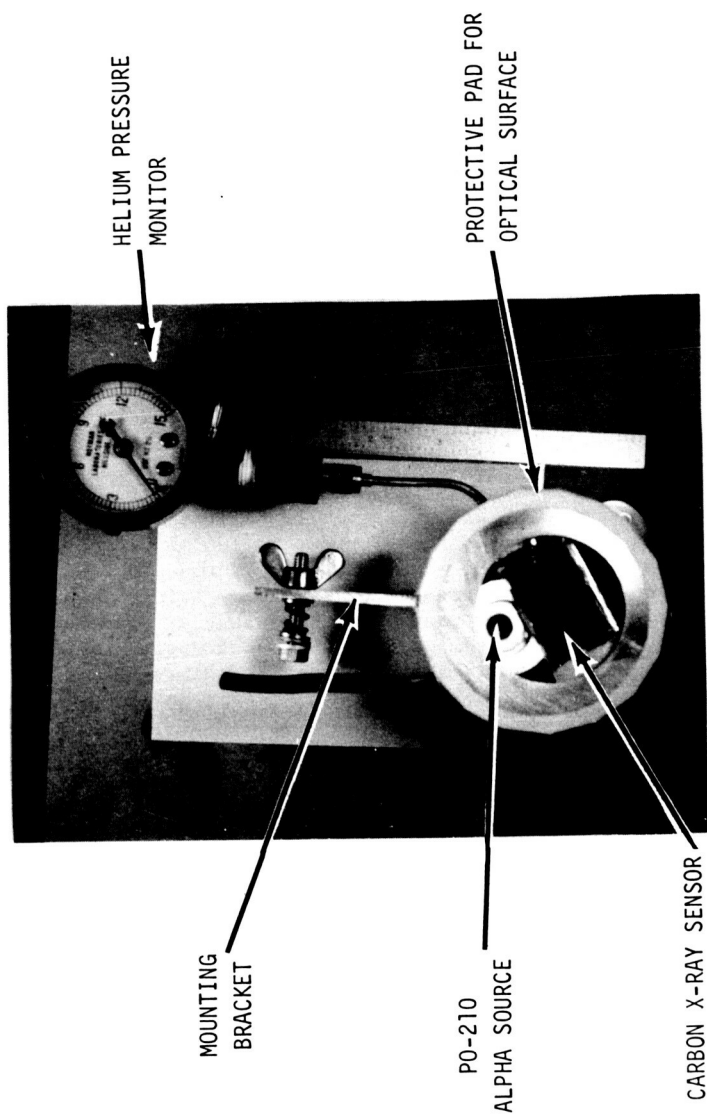


Figure 3, Photograph of Contamination Monitor  
Sensor Head

The instrumental background is created by the x-ray sensor itself. The x-ray sensor unfortunately has a very poor low energy x-ray resolution and therefore cannot completely isolate the carbon x-ray energy. The sensor retains a degree of sensitivity to those elements that comprise the mirror itself, such as oxygen, silicon, nickel, beryllium or gold. It is this detected x-ray counting rate to these mirror elements that gives the instrumental background rate. This background, however, is reproducible, stable and is such as not to interfere with the organic film measurements as shown by the measurements of Figure 4.

The mass per unit area of the polymer films is equal to the natural logarithm of the intensity transmission divided by the mass absorption coefficient of the materials for the measuring x-ray wavelength. The mass absorption coefficients for formvar at  $31.68^\circ$  is  $19300 \text{ cm}^2/\text{gm}$ <sup>(6)</sup> and that for polypropylene is  $21700 \text{ cm}^2/\text{gm}$ <sup>(6)</sup>. Based on these values of mass absorption coefficient and measured x-ray transmissions, the formvar films thicknesses are as follows; No. 2 -  $250^\circ$ , No. 3 -  $700^\circ$ , No. 4 -  $1600^\circ$  and the polypropylene film No. 5 -  $11300^\circ$ . The alpha-particle excited carbon -K $\alpha$  x-ray count ratio from each of the calibrated films was then measured, both for the case of an unbacked film and with the film coating a glass microscope slide substrate. The results are plotted in the form of a calibration curve in Figure 4. The minimum detectable contamination film thickness is determined by the  $3\sigma$  statistical variations in the instrumental background counting rate. From Figure 4 the background counting rate was 34,000 counts/100 seconds, which yields a  $3\sigma$  limit of  $\pm 600$  counts/100 seconds. Again from Figure 4, a hydrocarbon film of about  $50^\circ$  in thickness will give an increase in the background counting rate of about 1000 counts/100 seconds and is therefore fully detectable.

The chemical structure of formvar is  $(\text{C}_5\text{H}_7\text{O}_2)_x$  or about 35% carbon by atom density. Polypropylene is  $(\text{CH}_2)_x$  or about 33% carbon by atom density. These films then are believed to be fairly representative in terms of behavior to those condensed hydrocarbon contaminants on cold mirror surfaces.

#### Contamination Measurements of the Critical Surface on the Nimbus 5 Spacecraft

The contamination sensor was developed expressly to be used as a monitor for maintaining quality control of cleanliness for the Temperature Humidity Infrared Radiometer (THIR) scan mirror and the thermal control surface of the Electrically Scanning Microwave Radiometer (ESMR) on the Nimbus 5 spacecraft, successfully launched in December 1972.

#### Contamination Measurements of the THIR Scan Mirror

Figure 5 shows a photograph of the contamination sensor,

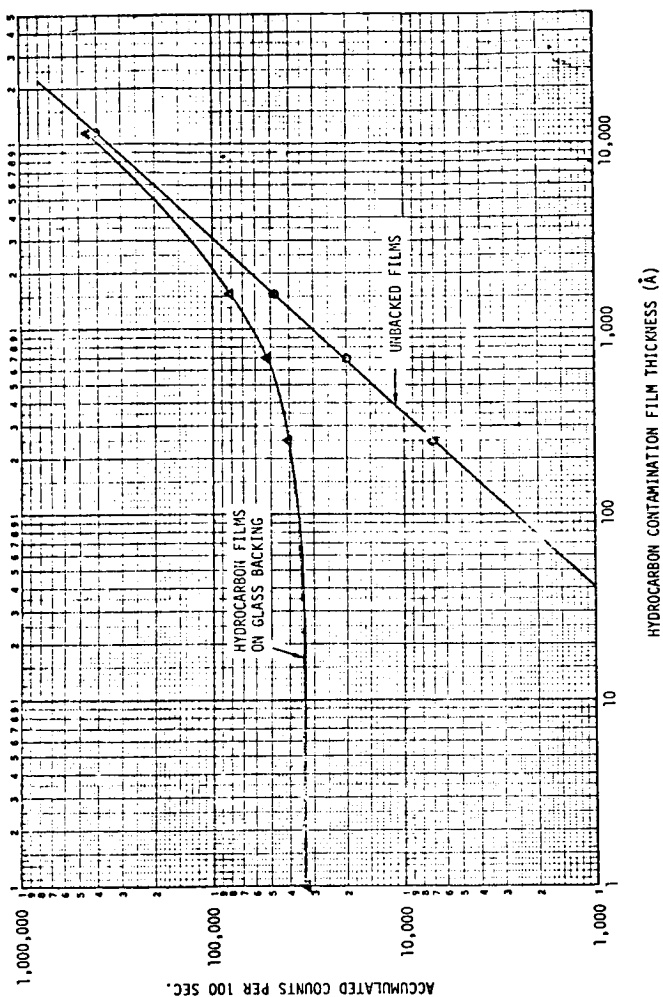


Figure 4, Contamination Sensor Calibration Curve  
(Hydrocarbon Film Thickness As A Function of Sensor Count Rate Based On Films  
Of 35% Carbon By Atomic Density)



mounted tripod and processing electronics. The tripod on which the sensor head is mounted provides three degrees of motion such that the sensor head can be carefully and accurately positioned to the surface to be examined assuring full protection to the critical surface. In addition, a lense tissue covered pad is provided on the sensor head to protect the mirror surface from a accidental contact with the sensor head. The necessary processing electronics consists of a high voltage power supply to energize the x-ray sensor, a pre-amp and amplifier, single-channel pulse height analyzer and pulse counter. Figure 6 and 7 are photographs of the contamination sensor being positioned to the scan mirror of the THIR experiment on the Nimbus E spacecraft for contamination measurements. Measurements were taken on four areas of the scan mirror, the center, left of center, right of center, and below center or bottom section of scan mirror. Measurements were made before cleaning, after cleaning and after cleaning a second time. The results are shown in Table II.

The results show that there was about a 10% difference in the counting rates before and after cleaning the THIR scan mirror, indicating hydrocarbon contamination was removed from the mirror surface. Measurements after a second cleaning showed no further changes to the counting rate level, indicating either all contamination was removed, or all that could be removed by the particular cleaning procedure used. The cleaning procedure used consisted of wiping the mirror with a pre-extracted lens tissue soaked in acetone followed by a second wiping of the mirror using a pre-extracted lens tissue soaked in isopropyl alcohol. Assuming the mirror contamination to be similar chemically to those films used for sensor calibration, then referring to Figure 4, a 4000 to 6000 counts/100 second rate corresponds to a contaminant film of about 200A° in thickness was removed from the THIR scan mirror surface. Figure 8 shows the pulse height energy spectrum obtained with the contamination monitor before and after cleaning of the THIR scan mirror.

#### Contamination Measurements of the Gold Kapton Thermal Control Surface of the ESMR

Measurements were taken on the gold Kapton tape covering the two main support areas of the ESMR. Two areas were measured on each support area. No additional cleaning of these surfaces were undertaken. The results are shown in Table III.

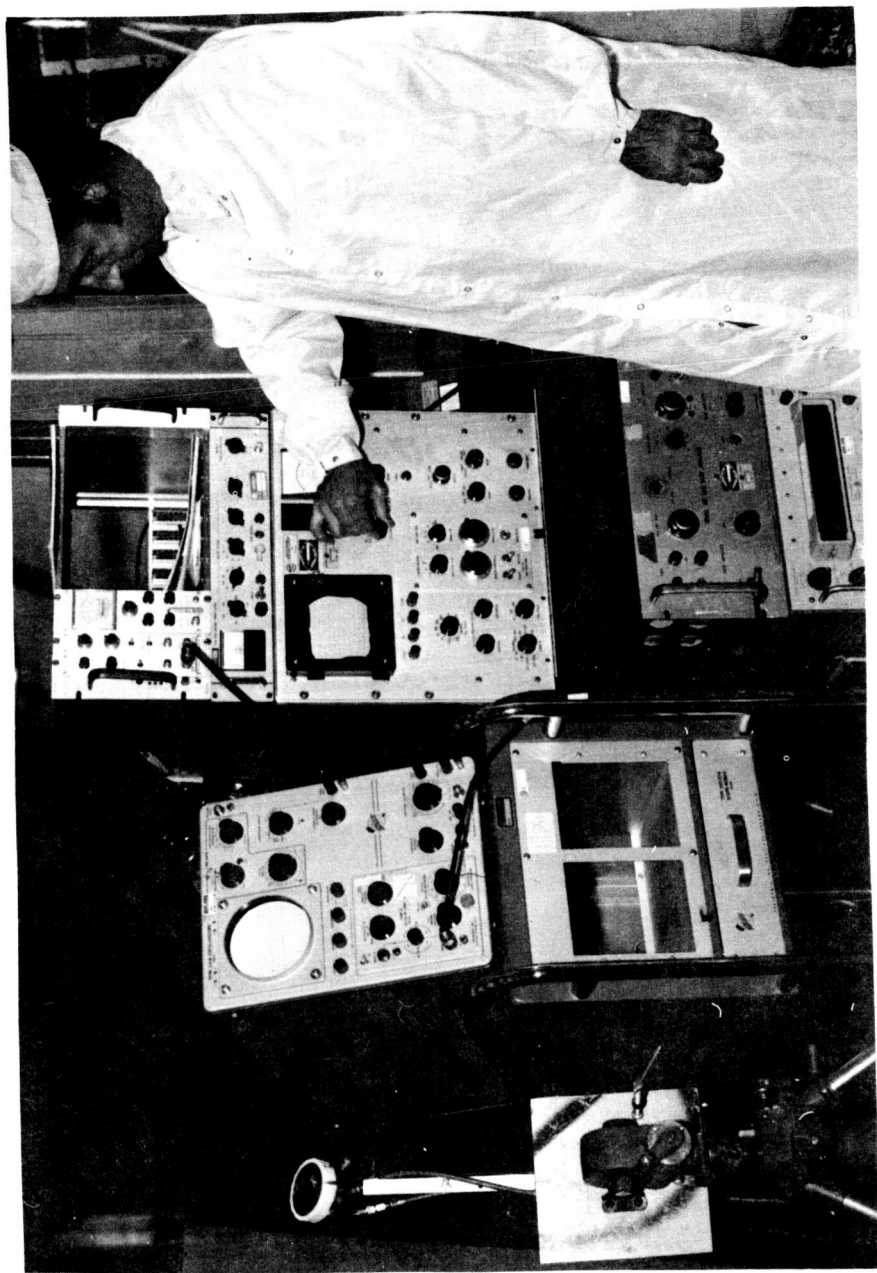


Figure 5, Photograph of the Contamination Sensor, Mounting Tripod and Processing Electronics



Figure 6, Photograph of Contamination Sensor Being Positioned to the Scan Mirror of the THIR Experiment on the Nimbus E Spacecraft

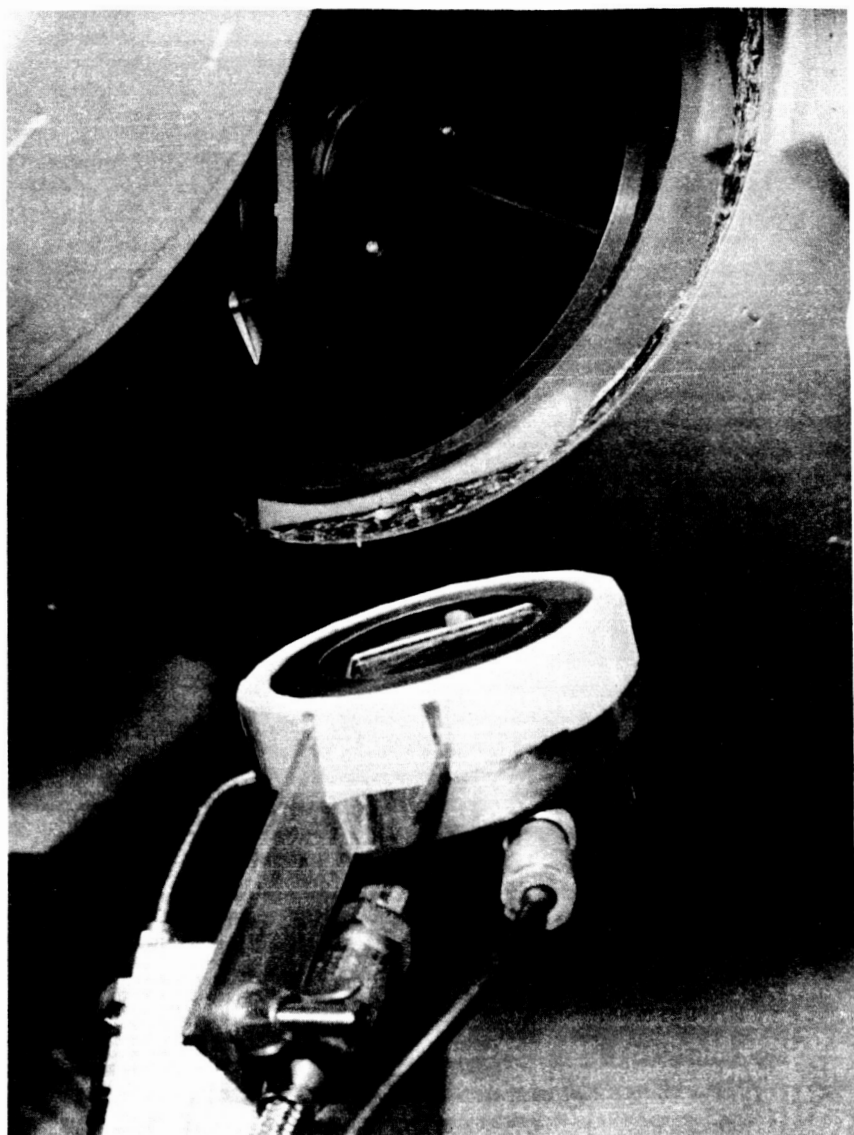


Figure 7, Close-up of Contamination Sensor

Table II

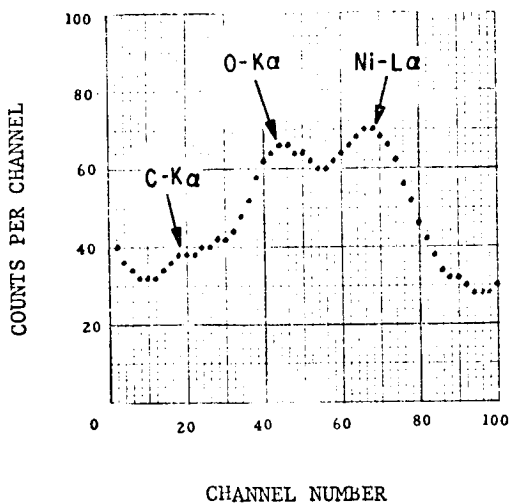
Measured X-Ray Counting Rate From THIR Scan Mirror  
(Counts per 100 seconds)

<u>Section</u>	<u>Before Cleaning</u>	<u>After Cleaning</u>	<u>Difference</u>	<u>After 2nd Cleaning</u>	<u>Difference</u>
Center	49893	45395	4498		
Left Center	48726	43971	4755		
Right Center	49266	44987	4279		
Below Center	50897	44832	6065	44921	00

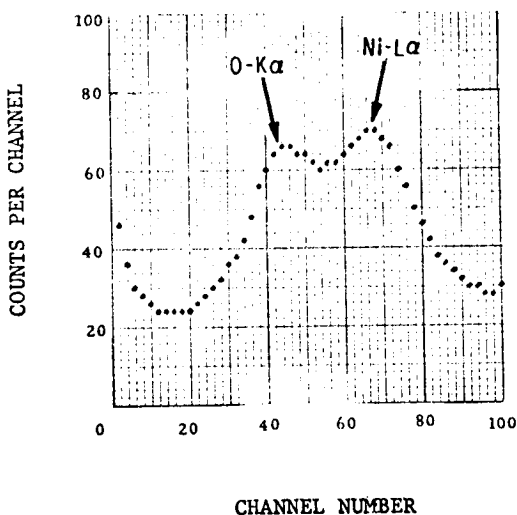
Table III

Measured X-Ray Counting Rates From the Gold Kapton on the ESMR  
(Counts per 100 seconds)

Left ESMR Support Area (looking at ESMR)	top section	33938
	bottom section	35211
Right ESMR Support Area	top section	36730
	bottom section	34284
Fresh Sample of Gold Tape		33840
Fresh Sample with <u>one</u> finger print stamped		43910
Fresh sample with finger print removed with isopropyl alcohol and cotton swab		34240



The Energy Distribution of X-Rays Emitted From The THIR Mirror When Excited by Alpha-Particles, Before Cleaning. (The oxygen and nickel x-rays lines are generated from the composition of the THIR mirror itself).



The Energy Distribution of X-Rays Emitted From The THIR Mirror After Cleaning. (Note the disappearance of the carbon x-rays from the condensed contamination.)

Figure 8, Pulse Height Energy Spectrums Obtained From Examination of The THIR Mirror With The Contamination Monitor

A fresh sample of the gold Kapton tape was used to establish the baseline counting rate of a "clean" gold Kapton surface for comparison. The results, using the fresh sample as a basis of comparison, shows that there are some areas on the ESMR support structure that have retained a degree of contamination. Referring to Figure 4, these areas of contamination measured about  $100\text{\AA}$  in thickness. As a further indication of the sensor sensitivity, a single finger print was placed on the fresh gold tape sample used as a reference and measured. The results (Table III) showed a 30% increase in the x-ray counting rate establishing extreme sensitivity even to a single finger print. The finger print was then "cleaned" from the gold tape sample. The measured results showed that the x-ray counting rate returned to the original level within the experimental error. The results also show just how effective a particular cleaning technique is or can be in removing condensed contamination from a particular surface.

In order to determine and maintain the cleanliness of a critical surface using the x-ray fluorescence contamination monitor, the baseline x-ray counting rate of the surface should be established prior to its subjection to any possible contamination. Measurement of the surface before and after exposure to a possible contaminating environment will then permit comparison to the baseline rate and enable quick detection of contaminants. Upon contamination and cleaning of the surface via an established cleaning procedure, the measurement technique can be re-employed to ascertain that the contaminant has been totally removed.

#### Thermal Vacuum Contamination In-Situ Measurement

In conjunction with the Nimbus F and ERTS B Contamination Programs, it was proposed to expand the existing thermal-vacuum contamination measurement capability to include two identical instruments known as the X-Ray Fluorescence Contamination Monitors modified for vacuum operation.

Contamination measurements within the thermal-vacuum chamber in the past had been limited to data taken from witness mirrors and from quartz crystal microbalance monitors. Witness mirrors provide information only after termination of the test. The quartz crystal microbalance (QCM) is very effective in measuring film thicknesses of metals and some inorganics in the range from  $100\text{\AA}$  to above  $10,000\text{\AA}$ . However, experience at GE, using QCM's as polymer contaminant crystal monitors for thermal vacuum testing of the Nimbus 5 spacecraft, show that the devices were only effective when polymer films exceeded some  $500\text{\AA}$  in thickness and when their temperature was maintained very constant. Another drawback in using the QCM technique is that condensate thickness is measured on the crystal surface, per se, and the sticking coefficient between the outgassed species and the QCM might be quite different from the condenser surface under investigation.

The X-Ray Fluorescence Contamination Monitor has the capability of monitoring absolute levels of contamination on a true optical surface and because of its digital nature, is free of environmental problems inherent in the quartz crystal monitor.

It was originally intended to design the Fluorescence Monitor so that it could measure the contamination level on a critical surface of the spacecraft (experiment). Because of mechanical, safety, and other considerations, the design was dropped, and it is proposed to fabricate and use the Fluorescence Monitor as a replacement for the quartz crystal monitor, i.e., to measure contamination levels in the proximity of the spacecraft experiments and critical thermal control surfaces.

### Instrument Description

The sensor head of the In situ X-Ray Fluorescence Contamination Monitor consists of a thin window proportional counter and an alpha-particle source. The source is a 0.375 inch disk of polonium 210 of 5 millicurie strength located in the center of the proportional counter window. The counter window consists of a 9-micron thick polypropylene aluminized films supported by a 75% transmitting aluminum wire mesh. The diameter of the window is 2 inches. The detected carbon X-rays are isolated by energy discrimination in the proportional counter. An integrated circuit preamplifier is used to amplify the pulses from the counter which are delivered outside the vacuum system to the remainder of the processing electronics.

The mechanical design of the instrument is presented in Figure 9. The witness mirror is rotated from the open position ninety degrees to accurately position the mirror beneath the sensor head for condensate contamination film measurement. Upon completion of the measurement, the mirror will be rotated to the open position for the continuation of contaminate collection.

The witness mirror will also be equipped with a heater and thermocouple to provide the capability of setting collector temperature to levels other than that of LN<sub>2</sub>.

A secondary witness mirror is also provided which is not exposed to the contaminate environment. This secondary witness mirror is used to establish and maintain the background baseline count rate. This mirror is measured when the primary mirror is in the open position.

### Experimental Check-Out of the X-Ray Sensor

On April 20, 1973 an experiment was initiated to establish that the proposed x-ray sensor for the Vacuum X-Ray Fluorescence Contamination Monitor would not only survive the vacuum environment, but also remain operational throughout a typical thermal vacuum test period of between 250 and 400 hours continuously.



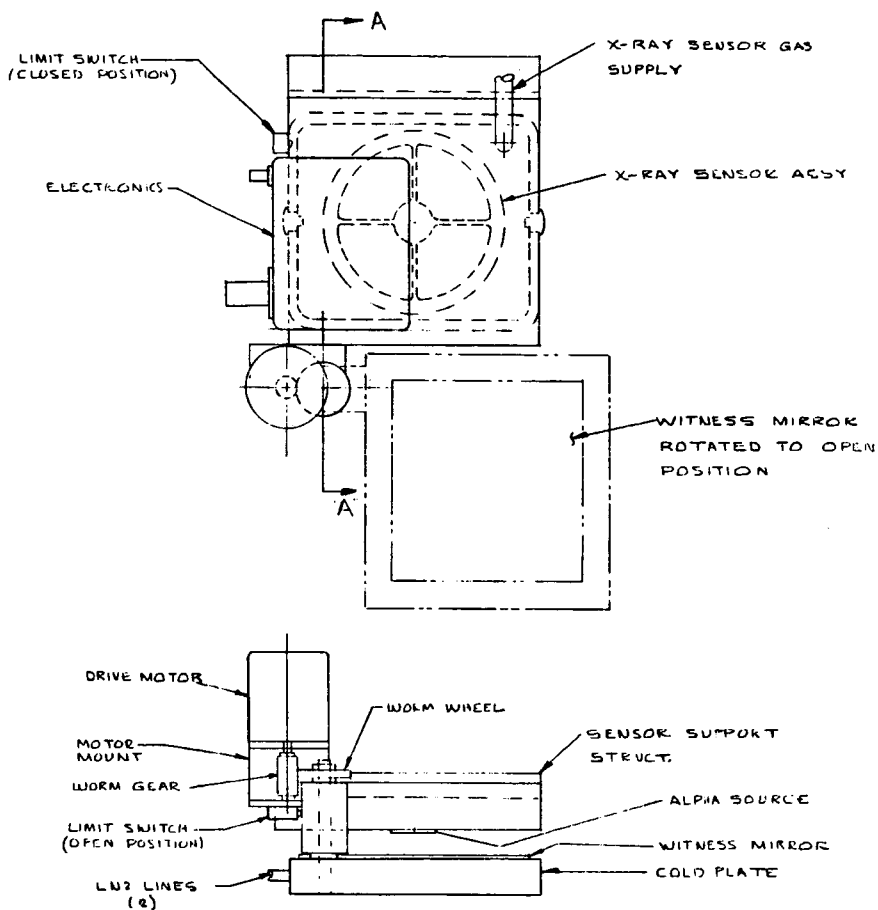


Figure 9, Mechanical Design Of The Vacuum X-Ray Fluorescence Contamination Monitor

The system performance criteria was based on maintaining system gain to within 50% and pulse-height energy resolution to within  $\pm 20\%$  of the original values before vacuum testing as established with a test source.

The proportional counter used, although not identical in geometry and construction as the unit proposed, is adequately representative of the design. The counter consists of sealed metal cylinder with an epoxied thin x-ray entrance window. The window consists of a 9-micron thick polypropylene film supported by a 75% transmitting aluminum wire mesh. A 50 microcurie Iron 55 radioisotope x-ray source was used to simulate the x-ray flux to the sensor. The entire system was placed in a Materials Engineering vacuum chamber and maintained continuously at a pressure below  $10^{-6}$  torr. The sensor performed satisfactorily with gain increase of 30% and no measurable change to the pulse-height resolution for a period of more than 1100 hours.

Based on this experiment then, one should expect reasonable success for the actual vacuum units when they are completed. The thermal vacuum tests for the Nimbus F spacecraft are scheduled for early 1974.

#### CONCLUSION

It has been shown experimentally through calibration of actual thin hydrocarbon films that the charged particle excited x-ray fluorescence contamination sensor is an extremely sensitive device for determining minute quantities of a condensed hydrocarbon surface contaminant on optical or thermal control surfaces.

The sensor itself is relatively inexpensive, reliable, accurate and relatively easy to use. It is small in size and requires no "special" electronic equipment. The device is non-destructive and non-interfering with the surface being investigated and it provides relatively quick detection of contamination. (A typical contamination measurement of a mirror surface such as the THIR scan mirror takes only an hour to an hour and a half, including the set-up time.) The sensor is stable and poses no radiation hazard to personnel or equipment. In addition, selected elements that make up the contaminating film can also be identified if desired, these include, beside carbon; oxygen, nitrogen, fluorine, sulphur, silicon, etc. The device however, does require operation either in a vacuum or a helium atmosphere.

In all the x-ray fluorescence contamination sensor makes a useful monitor for the detection and measurement of environmental contamination on critical surfaces either remotely or in-situ for the establishment and preservation of cleanliness.

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